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Synthesis of Aerogel-Metal Cluster Composites by Gamma Radiolysis

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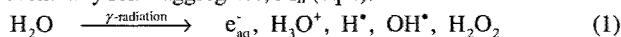Columbia, MO 65211, USA.

ABSTRACT

Noble metal clusters (Ag, Au) were formed in a silica aerogel matrix by gamma irradiation of hydrogel precursors loaded with aqueous solutions containing Ag^+ or $[AuCl_4]^-$ ions. Hydrogels exposed to gamma rays assumed the color expected for colloidal suspensions of Ag (respectively Au) clusters. The hydrogels were subsequently washed and supercritically dried, without any evident change in color, indicating that the metal clusters were not removed during drying. Typical gamma ray doses were between 3 and 3.5 kGy, and achieved complete reduction of hydrogels containing metal ion concentrations in the 10^{-4}-10^{-3} M range. Metal clusters in the aerogel monoliths were characterized with optical absorption, transmission electron microscopy, X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. These techniques have shown that the clusters have a crystalline fcc structure. Au clusters consist of pure Au, while surface oxidation of Ag clusters was observed with XPS.

INTRODUCTION

In situ formation and entrapment of metal clusters in aerogels is desirable for application in catalysis[1,2], sensors[3], waste disposal[4,5], and electromagnetic shielding. Metal clusters have been formed in aerogels by adding to a hydrogel a precursor, generally an organometallic compound that does not leach out during the wash cycles required prior to the final supercritical drying procedure. High temperature treatment of the dry aerogel leads to reduction and deposition of the metal particles.[1,2] Alternatively, colloidal metal particles have been added directly into the sol during gelation, and remain trapped all the way to the final aerogel.[6,7]

Another efficient method of reducing metal ions to form homo- and heteronuclear clusters of transition metals is via gamma radiolysis of aqueous solutions.[8-15] That process is initiated by formation of solvated electrons, e_{aq}^- (eq 1), which reduce metal ions M^{m+} to metal atoms (eqs 2, 3). Metal atoms eventually form aggregates, M_n (eq 4).

$$H_2O \xrightarrow{\gamma\text{-radiation}} e_{aq}^-, H_3O^+, H^\bullet, OH^\bullet, H_2O_2 \qquad (1)$$

$$e_{aq}^- + M^{m+} \longrightarrow M^{(m-1)+} \qquad (2)$$

$$e_{aq}^- + M^+ \longrightarrow M_0 \qquad (3)$$

$$nM_0 \longrightarrow M_2 \longrightarrow \ldots\ldots M_n \qquad (4)$$

In this paper we describe the formation of nanoscopic metal clusters induced by gamma irradiation of a hydrogel in which the gelation solvent (CH_3OH) has been exchanged by an aqueous solution containing ions of the desirable metal (Ag and Au). Typical work-up of the resulting metal cluster embedded hydrogels leads to aerogel-noble metal cluster nanocomposites. The materials were characterized with optical absorption, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Our results show that the noble metal clusters have crystalline fcc structure with lattice parameters comparable to those of the bulk materials, and a cluster size distribution between 10 and 200 nm. Au clusters are free of contamination, while surface oxidation of the Ag clusters has been observed.

The main advantage of our technique is its versatility. For example, it is known that radiolysis allows formation of non-equilibrium alloy clusters such as Au cores surrounded by a Ag shell.[9] Such structures are not accessible by simple impregnation methods, where cluster formation is achieved through high temperature treatment, which leads to equilibrium structures. Furthermore, radiolysis can be used to synthesize clusters out of a wide array of noble and transition metals, like Ni, Co, and Pb.[10]

Experimental Details

Silica aerogel composites were prepared by a modification of previously published procedures in which the contents of vial A (4.514 mL of tetramethoxysilane; 3.839 mL of methanol) and of vial B (4.514 mL of methanol; 1.514 mL of water, and 20 µL of concentrated NH_4OH) are mixed thoroughly to form a sol that gels at room temperature in 10-15 min.[3] The gels were left to age at room temperature then were removed from their molds and soaked in water. The water-washed gels were washed again, with an aqueous solution of the desired metal ion. Such solutions were prepared using $AgNO_3$, $HAuCl_4$, and 2-propanol. The metal ion concentrations varied from 10^{-4} M to 1 M. 2-propanol was added with a typical concentration of 0.2 M to scavenge the $H^\bullet$ and $OH^\bullet$ radicals generated during irradiation, eq 1. After the fourth washing, the solution surrounding the gels was decanted. The vials were closed tightly to avoid loss of solvent (water) by evaporation, and they were placed in close proximity of the core of the campus nuclear reactor. At the end of the irradiation period, the gels were visibly darker (depending on the concentration and chemical identity of the metal ions). The vials were filled with water and the gels were allowed to equilibrate for 12 hrs. Subsequently, the metal-impregnated gels were washed with acetone. The pore-filling acetone was removed by supercritical drying with CO_2.[3]

The samples were irradiated with γ radiation from the fission products of the campus' nuclear reactor (a pool reactor with a maximum power of 200 kW that employs ^{235}Ur fuel rods.) Typical total doses were up to about 3.5 kGy per run, as measured by Thermoluminescent Dosimeters (TLD) placed in vials adjacent to those containing the samples. Typically, gamma rays yield 6 solvated electrons per 100 eV of deposited energy, or, equivalently, 6×10^{-7} M per joule of adsorbed energy. Thus, a dose of 1 kGy can reduce about 5.7×10^{-4} M of Ag^+, and our typical doses of 3-3.5 kGy achieved 100% metal ion reduction for Ag^+ samples with a concentration below about 2×10^{-3} M. Alternatively, a few samples were irradiated with a ^{60}Co source located at University of Missouri-Columbia, which generates dose rates of about 18 kGy/h. It was employed to prepare aerogel/cluster composites with high metal concentrations, whose reduction would otherwise require an excessively long time.

Optical absorption was measured with a Cary 500 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis 165 scanning spectrometer equipped with a 225 Watt Mg monochromatized X-ray source. Surveys were taken over areas as large as 120 square microns to ensure that noble metal clusters were distributed uniformly throughout the aerogel volume. X-ray diffraction (XRD) was measured with a Scintag PadX diffractometer (with a Cu Kα source). Transmission electron microscopy (TEM) was carried out with a Philips EM430T microscope, operated at 300 keV. Selected area electron diffraction (SAED) was used to characterize cluster structure and determine lattice parameters. Local chemical composition was determined with energy dispersive X-ray chemical analysis (EDS). BET surface area measurements were carried out with a Quantachrome Autosorb-1 instrument.

DISCUSSION

Gamma irradiation deeply affects the color of metal-loaded hydrogel monoliths. Hydrogels with low metal concentrations (10^{-4} to 10^{-2} M) irradiated with gamma rays (mostly from Source A) assume the typical color of colloidal suspensions of metal clusters, i.e., pink for Au, brownish for Ag. Hydrogels with higher metal concentration ($\geq 10^{-1}$ M) become opaque. The color of the monoliths does not change after supercritical drying, indicating that the metal clusters are firmly embedded in the silica matrix. Table 1 shows properties of several aerogels containing varying concentrations of Ag and Au.

Reduced Amount (M)	Metal	Density (g/cm³)	Surface Area (m²/g)	Mean pore diameter (nm)	Monolith Color	Metal Loading (%w/w)
10^{-4}	Ag	0.108	734±100	8.24±1	Brown	0.01
10^{-3}	Ag	0.108			Dark Brown	0.1
0.18	Ag	0.128	776±100	6.80±1	Opaque	15
1	Ag	0.1347			Opaque	75
10^{-4}	Au	0.116			Pink	0.02
10^{-4}	Au	0.133	879±100	9.62±1	Pink	0.015
10^{-3}	Au	0.156			Pink	0.126

Table 1. Densities, surface areas, and mean pore diameter of aerogel composites loaded with Ag and Au at different concentrations.

The structure of the aerogels was not fundamentally affected by the synthesis procedure, or by the presence of the clusters. In SEM micrographs of the Ag-aerogel composites, the bead structure of silica is evident, and similar to that reported for native silica aerogels.[3] The density values of the metal doped aerogels are larger, but still comparable with those of pure silica aerogels (0.003-0.010 g/cm³).[7] Surface areas and mean pore sizes are in the 700-900 m²/g and 7-10 nm range respectively, close to the values reported for native silica aerogels (700-1000 m²/g and, 8-14 nm, respectively).[3,7,19,20]

Figure 1 shows typical optical absorption spectra of Au- and Ag-loaded silica aerogel monoliths. The absorption maximum of the Ag-doped aerogels is at 385 ± 2 nm, while the maximum of the Au-doped aerogels is at 518 ± 2 nm. These values lie within the range of values previously reported for the plasmon absorption of Au and Ag metal clusters,[18,19] and confirm

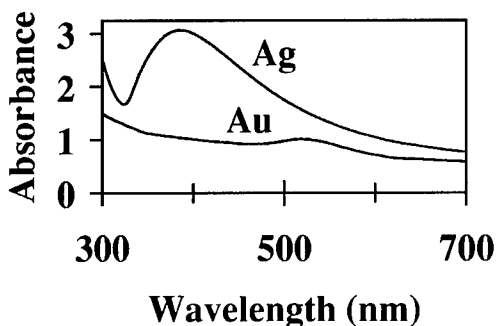the presence and chemical identity of metal clusters in both irradiated hydrogel and aerogel composites.

Figure 2. Optical absorption of Ag- and Au- doped aerogel composites obtained by irradiation with Source A of hydrogels made out of solutions having concentrations $[Ag^+] = 10^{-4}$ M, and $[Au^{III}] = 10^{-4}$ M, respectively.

TEM images of Ag- and Au-loaded silica aerogels are reported in Figure 4. Figure 4a shows several metal particles embedded in a large silica flake. SAED and EDS showed that the metal clusters are free of contamination, and have fcc structure. Size distributions of metal particles were determined by measuring a large number of particles from several different images. These are reported in Figure 4b-d for Ag^+ concentrations in the bathing solutions varying from 10^{-4} M to 0.18 M. The mean particle size increases with increasing $[Ag^+]$, from about 45 nm at 10^{-4} M to about 65 nm at 5×10^{-2} M, to about 170 nm at 0.18 M. This particle size dependence on concentration is an indication that cluster growth dominates on cluster nucleation, i.e., nuclei form in the initial stages of reduction, and keep growing, without any (or few) new nuclei being added. Figure 4e shows the size distribution of a sample originating from a solution with $[Au^{III}] = 10^{-4}$ M. Particles are somewhat smaller than those in the Ag sample coming from the same bath concentration, and the mean Au particle size is about 30 nm.

XPS analysis of a 0.5 M $[Ag^+]$ aerogel revealed the binding energy of the $3d$ states is shifted towards lower energies compared to the bulk. Such shifts are characteristic of oxidized Ag species.[22] Ag oxidation is understandable, considering that the supporting matrix is an oxide and that the synthesis mechanism proceeds, in basic medium, via an Ag_2O intermediate.[21] Oxide states are probably superficial, since XRD analysis is consistent with a fcc structure with the lattice parameter of bulk Ag.
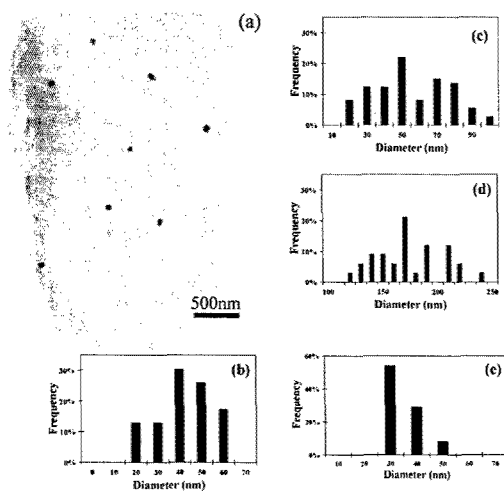
Figure 4. (a) Bright field TEM micrograph of a 5.7×10^{-2} M [Ag$^+$] aerogel. (b) Size distribution histogram of a 10^{-4} M [Ag$^+$] aerogel (23 particles measured). (c) Size distribution of a 5.7×10^{-2} M [Ag$^+$] aerogel (73 particles measured). (d) Size distribution histogram of a 0.18 M [Ag$^+$] aerogel (25 particles measured). (e) Size distribution histogram of a 10^{-4} M [Au^{III}] aerogel (24 total particles). Samples irradiated with UMR reactor

CONCLUSION

In conclusion, we have described a method for the synthesis of metal cluster/aerogel composites. The new materials retain the characteristics of aerogels with a metal content of up to 75% w/w. Work is under way to demonstrate the ability of our method to synthesize clusters of non-noble metals, like Ni, and alloys. These are well known characteristics of the radiolysis technique, and can be employed to tailor the physical and chemical properties of aerogel/metal composites.

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